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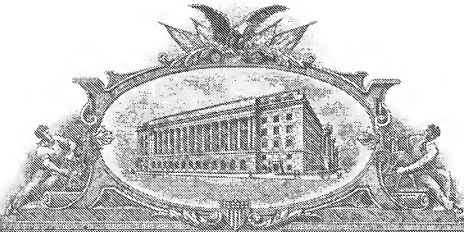
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FILING DATE: *December 05, 2003*

RELATED PCT APPLICATION NUMBER: PCT/US04/40629



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<b>UTILITY PATENT APPLICATION TRANSMITTAL</b>	<b>Attorney Docket No.</b> 52993-285536 <b>First Inventor</b> David Forrest and Mark Schauer <b>Title</b> Articles Formed By Chemical Vapor Deposition and Methods for Their Manufacture <b>Express Mail Label No.</b> EV 015610683 US
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(Only for new nonprovisional applications under 37 C.F.R. 1.53(b))

<b>APPLICATION ELEMENTS</b> See MPEP chapter 600 concerning utility patent application contents.	<b>ADDRESS TO:</b> Mail Stop Patent Application Commissioner for Patents P.O. Box 1450 Alexandria VA 22313-1450
1. <input checked="" type="checkbox"/> Fee Transmittal Form (e.g., PTO/SB/17) <i>(Submit an original and a duplicate for fee processing)</i> 2. <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. 3. <input checked="" type="checkbox"/> Specification [Total Pages <span style="border: 1px solid black; padding: 0 5px;">29</span> ] <i>(preferred arrangement set forth below)</i> - Descriptive title of the invention - Cross Reference to Related Applications - Statement Regarding Fed sponsored R & D - Reference to sequence listing, a table, or a computer program listing appendix - Background of the invention - Brief Summary of the invention - Brief Description of the Drawings (if filed) - Detailed Description - Claim(s) - Abstract of the Disclosure 4. <input checked="" type="checkbox"/> Drawing(s) (35 U.S.C. 113) [Total Sheets <span style="border: 1px solid black; padding: 0 5px;">8</span> ] 5. Oath or Declaration [Total Sheets <span style="border: 1px solid black; padding: 0 5px;">3</span> ] a. <input checked="" type="checkbox"/> Unexecuted (original or copy) b. <input type="checkbox"/> Copy from a prior application (37 CFR 1.63 (d)) <i>(for a continuation/divisional with Box 18 completed)</i> i. <input type="checkbox"/> <b>DELETION OF INVENTOR(S)</b> Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b). 6. <input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76	7. <input type="checkbox"/> CD-ROM or CD-R in duplicate, large table or Computer Program (Appendix) 8. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary) a. <input type="checkbox"/> Computer Readable Form (CRF) b. Specification Sequence Listing on: i. <input type="checkbox"/> CD-ROM or CD-R (2 copies); or ii. <input type="checkbox"/> Paper c. <input type="checkbox"/> Statements verifying identity of above copies <b>ACCOMPANYING APPLICATIONS PARTS</b> 9. <input type="checkbox"/> Assignment Papers (cover sheet & document(s)) 10. <input type="checkbox"/> 37 C.F.R. 3.73(b) Statement of Attorney <i>(when there is an assignee)</i> 11. <input type="checkbox"/> English Translation Document (if applicable) 12. <input type="checkbox"/> Information Disclosure Statement (IDS/PTO-1449) <input type="checkbox"/> Copies of IDS Citations 13. <input type="checkbox"/> Preliminary Amendment 14. <input checked="" type="checkbox"/> Return Receipt Postcard (MPEP 503) <i>(Should be specifically itemized)</i> 15. <input type="checkbox"/> Certified Copy of Priority Document(s) <i>(if foreign priority is claimed)</i> 16. <input type="checkbox"/> Nonpublication Request under 35 U.S.C. 122 (b)(2)(B)(i). Applicant must attach form PTO/SB/35 or its equivalent. 17. <input checked="" type="checkbox"/> Other: - Check in amount of \$806

18. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment, or in an Application Data Sheet under 37 CFR 1.76:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No: \_\_\_\_\_ / \_\_\_\_\_  
 Prior application information: Examiner: \_\_\_\_\_ Art Unit: \_\_\_\_\_

For CONTINUATION or DIVISIONAL APPS only: The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 5b, is considered a part of the disclosure of the accompanying or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

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Name (Print/Type)	Dean W. Russell	Registration No. (Attorney/Agent)	33,452
Signature	<i>Dean W. Russell</i>	Date	December 5, 2003

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**FEE TRANSMITTAL  
for FY 2004**

Effective 10/01/2003. Patent fees are subject to annual revision.

☐ Applicant claims small entity status. See 37 CFR 1.27**TOTAL AMOUNT OF PAYMENT** (\$) 806**Complete if Known**

Application Number	Express Mail Label EV 015610683 US
Filing Date	December 5, 2003
First Named Inventor	David Forrest and Mark Schauer
Examiner Name	Not yet assigned
Art Unit	Not yet assigned
Attorney Docket No.	52993-286536

**METHOD OF PAYMENT (check all that apply)**
☒ Check ☐ Credit card ☐ Money Order ☐ Other ☐ None
☒ Deposit Account:

Deposit Account Number	11-0855
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Deposit Account Name	Kilpatrick Stockton LLP
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The Director is authorized to: (check all that apply)

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**FEE CALCULATION****1. BASIC FILING FEE**

Large Entity		Small Entity		Fee Description	Fee Paid
Fee Code	Fee (\$)	Fee Code	Fee (\$)		
1001	770	2001	385	Utility filing fee	770
1002	340	2002	170	Design filing fee	
1003	530	2003	265	Plant filing fee	
1004	770	2004	385	Reissue filing fee	
1005	160	2005	80	Provisional filing fee	

SUBTOTAL (1)

(\$ 770)

**2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE**

Total Claims		Extra Claims		Fee from below		Fee Paid	
22	-20 **	2	X	18	=	36	
Independent Claims							
2	-3 **	0	X		=	0	
Multiple Dependent							
			X		=	0	

Large Entity		Small Entity		Fee Description
Fee Code	Fee (\$)	Fee Code	Fee (\$)	
1202	18	2202	9	Claims in excess of 20
1201	85	2201	43	Independent claims in excess of 3
1203	290	2203	145	Multiple dependent claim, if not paid
1204	86	2204	43	** Reissue independent claims over original patent
1205	18	2205	9	** Reissue claims in excess of 20 and over original patent

SUBTOTAL (2)

(\$ 36)

\*\*or number previously paid, if greater, For Reissues, see above

**FEE CALCULATION (continued)****3. ADDITIONAL FEES**

Large Entity Small Entity

Fee Code	Fee (\$)	Fee Code	Fee (\$)	Fee Description	Fee Paid
1051	130	2051	65	Surcharge - late filing fee or oath	
1052	50	2052	25	Surcharge - late provisional filing fee or cover sheet	
1053	130	2053	65	Non-English specification	
1812	2,520	1812	2,520	For filing a request for reexamination	
1804	920*	1804	920*	Requesting publication of SIR prior to Examiner action	
1805	1,840*	1805	1,840*	Requesting publication of SIR after Examiner action	
1251	110	2251	55	Extension for reply within first month	
1252	420	2252	210	Extension for reply within second month	
1253	950	2253	475	Extension for reply within third month	
1254	1,480	2254	740	Extension for reply within fourth month	
1255	2,010	2255	1,005	Extension for reply within fifth month	
1401	330	2401	165	Notice of Appeal	
1402	330	2402	165	Filing a brief in support of an appeal	
1403	290	2403	145	Request for oral hearing	
1451	1,510	1451	1,510	Petition to institute a public use proceeding	
1452	110	2452	55	Petition to revive - unavoidable	
1453	1,330	2453	665	Petition to revive - unintentional	
1501	1,330	2501	665	Utility issue fee (or reissue)	
1502	480	2502	240	Design issue fee	
1503	640	2503	320	Plant issue fee	
1460	130	1460	130	Petitions to the Commissioner	
1807	50	1807	50	Processing fee under 37 CFR 1.17 (q)	
1806	180	1806	180	Submission of Information Disclosure Stmt	
8021	40	8021	40	Recording each patent assignment per property (times number of properties)	
1809	770	2809	385	Filing a submission after final rejection (37 CFR § 1.129(a))	
1810	770	2810	385	For each additional invention to be examined (37 CFR § 1.129(b))	
1801	770	2801	385	Request for Continued Examination (RCE)	
1802	900	1802	900	Request for expedited examination of a design application	

Other fee (specify) \_\_\_\_\_

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SUBTOTAL (3)

(\$ 0)

**SUBMITTED BY**

Name (Print/Type)	Dean W. Russell	Registration No. (Attorney/Agent)	33,452
Signature	<i>Dean W. Russell</i>	Date	December 5, 2003

**Complete (if applicable)**

Telephone	404 815 6528
Date	December 5, 2003

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# **ARTICLES FORMED BY CHEMICAL VAPOR DEPOSITION AND METHODS FOR THEIR MANUFACTURE**

## **BACKGROUND**

### **1. Field of the Invention**

The invention relates to articles formed by chemical vapor deposition and methods of forming such articles.

### **2. Description of Related Art**

Chemical vapor deposition (CVD) techniques have been widely used to provide thin films and coatings of a variety of materials on various products. Typically, the process involves reacting vaporized or gaseous chemical precursors in the vicinity of a substrate to result in a material such as silicon carbide (SiC) depositing on the substrate. The deposition reaction is continued until the deposit reaches the desired thickness.

CVD techniques can be used to form relatively thin coatings on the surfaces of pre-existing articles; in this situation, the surface of the article forms the substrate. However, CVD techniques can also be adapted to produce articles that are formed from the deposited material. In this situation, the substrate upon which deposition occurs is a form or mandrel that provides an initial shape to the article. The article, which is removed after sufficient deposition has occurred, has a complimentary surface that corresponds to the form or mandrel. Such articles are called "free-standing" articles herein.

One method by which free-standing SiC articles are formed by CVD includes feeding silicon carbide precursor gases or vapors into a deposition chamber, where they are heated to a temperature at which they react to produce silicon carbide. The precursor gases or vapors react at the surface of a substrate or other structure loaded into or placed in the chamber. The silicon carbide builds up as a shell or a deposit on the substrate. Different articles may require different thicknesses, and thicknesses can range from less than 100 microns to over an inch or two inches thick. The thickness can be controlled by controlling the deposition time and/or other process variables. When the desired deposition thickness is reached, the mandrel or substrate is then removed from the deposition chamber and the deposited silicon carbide is separated therefrom.

In one method for forming SiC articles, methyltrichlorosilane ( $\text{CH}_3\text{SiCl}_3$  or MTS), hydrogen ( $\text{H}_2$ ), and argon (Ar) gases are introduced into the furnace through an injector. MTS is a liquid at ambient or room temperature, and sufficient vapor can be delivered into the reaction vessel by feeding carrier gas through the MTS liquid or by picking up vapor above the liquid. Gases that are unreacted in the furnace are pumped out by a vacuum pump, filtered, and cleaned in a gas scrubber before being vented to the atmosphere.

Some industries require thinly-formed silicon carbide rings or articles. The current technology of producing monolithic ceramic parts via the chemical vapor deposition process includes producing large sheets of the ceramic material in a CVD furnace. SiC is deposited onto a flat or box-shaped substrate to form the relatively large, flat sheets, from which the final ceramic part or parts are machined. The

machining process includes cutting the rough shape out of the large sheet, grinding the piece to near the desired thickness to produce a blank that approximates the final form but with surplus material thickness on each face, and then machining the blank to the dimensions of the final form.

When CVD materials are deposited on large flat substrates, the material exhibits a crystal growth that is perpendicular to the plane of the flat substrate. The material is not necessarily deposited evenly to form a sheet that is uniform in thickness or in microstructure, so that there may be thicker portions in some areas and thinner portions in other areas, instead of a uniform thickness throughout. Because the sheet typically has a thickness profile that is non-uniform, the thickness can vary between rings that are ultimately formed, depending upon where they were cut from the sheet. Moreover, the thickness within an individual ring may vary with position.

In addition, due to the large size of the SiC sheet from which the SiC rings are typically formed, different microstructures may exist at different areas of the sheet. For example, when a ring is produced from a sheet of deposited material, differences in the material characteristics across the thickness of the deposited sheet may lead to increased tension or stress within the material that can cause a slight axial bow or curve in the machined ring.

Another manifestation of the different microstructures across the large plate is a variation in cosmetic appearance across the final machined parts, e.g. rings. These variations in cosmetic appearance can be further magnified when the finished parts are coated with other vacuum deposited or vapor deposited coatings, especially CVD deposited coatings such as silicon.

Additionally, because of the thickness variations the CVD process time must be increased to bring the low deposition rate areas up to the minimum thickness requirements for the desired parts. The higher deposition rate areas then cause the pieces cut from the sheet to require more machining time in order to be ground to the required thickness.

Moreover, there is limited flexibility in the geometry of a sheet and the pieces to be cut, so there is material waste due to the layout pattern of the pieces. There is also surplus material in the piece pattern that is cut or ground from between and within the pieces to make the blanks, such as edges and centers of rings, which results in a large quantity of scrap material. For example, the material that is cut out around each ring and between each ring (to form an inner diameter of the ring) is typically wasted, much like the unused cookie dough remaining after cookies are stamped out from a roll of cookie dough.

There are also occasional problems with cracking of a large, CVD-produced plates or sheets of ceramic material during the CVD process, which can reduce the yield significantly. The combination of cracks and the scrap material from the sheet and the material that is ground from the blanks lowers the average raw material-to-product conversion ratio significantly.

An alternate method that has been used to manufacture silicon carbide rings includes mounting disk-like mandrel substrates through their respective centers in a spaced and parallel relationship in grooves on a shaft. The planar surfaces of the disk-like mandrel substrates are oriented perpendicular to the axis of the shaft.



During processing, the shaft is rotated as gases are injected into the chamber, such that ring-shaped ceramic parts are formed by deposition on the mandrel substrates.

A different but related method of creating silicon carbide rings is to suspend within a deposition chamber individual, flat graphite ring mandrels having an outside diameter and an inside diameter similar to those desired in the SiC rings. The gas mixture of MTS in hydrogen and argon is fed into the chamber and silicon carbide is deposited on the mandrels to form rings. Once the rings are removed from the graphite ring mandrels, their inner and outer diameter can be machined to the desired dimensions.

One problem related to forming silicon carbide rings from these alternative processes is that the mandrels need to be rotated throughout the formation process to prevent build-up in undesired areas. In many instances, the gases are injected into the reaction chamber such that the gases are not focused on any particular mandrel or surface of interest, but instead are allowed to deposit non-uniformly on all surfaces of the reactor. The rotation or suspension of the substrate in the reaction gas stream is intended to prevent or limit this non-uniformity of deposition.

The specifically-shaped mandrels are also complicated to manufacture. In the embodiment that includes a shaft with disk-shaped mandrels placed in grooves, the grooves must be specially machined for receiving and supporting the disk-shaped mandrel substrates. In the graphite ring embodiment, each ring support axis must have protrusions or tabs that facilitate their suspension or placement in the chamber, and material is often deposited in or around the protrusions or tabs.

Additionally, in each of the above-described methods, the resulting ring has a crystal growth that is oriented axially relative to the ring or finished article, not radially oriented relative to the ring or article. In other words, the microstructure contains grains oriented perpendicular to the plane of the finished part. Further, it is known that as materials are deposited by chemical vapor deposition the size of grains increases as the growth proceeds away from the substrate. The evolution in grain structure from small grains to large grains occurs as grains with lower energy crystallographic orientations grow faster than grains with less preferred orientations, under the particular deposition conditions used. This evolution of grain structure typically produces a gradient in microstructure across the thickness of the material, which in turn causes a gradient in internal stress of the deposited material, resulting in bending or "bow" of the deposited material when it is released from the substrate. This gradient in material microstructure and stress complicates the machining process, and remains in the material even after machining is completed, often resulting in some bow or waviness in the finished part. This bow or waviness is undesirable, especially in parts that require precise tolerances and extremely consistent flatness, such as rings for use in contact with semiconductor wafers. The larger the part, the more significant the problem can become.

Regardless of these difficulties and costs associated with manufacturing silicon carbide articles, silicon carbide has a unique combination of properties that make it a particularly suitable material for a variety of applications in the semiconductor, optical, electronic and chemical processing fields. Silicon carbide

articles produced by CVD processing are recognized to exhibit superior mechanical, thermal, physical and optical properties.

Accordingly, the present inventors have found a way to improve CVD processing for producing articles, in particular planar articles such as rings and discs, and more particularly silicon carbide ring-shaped articles. The resulting articles have a unique microstructural orientation relative to the shape of the article. The invention may also be used to create articles having other shapes. Such articles can be used in fixtures to support silicon and other wafers for processing, susceptor rings for supporting wafers in semiconductor furnaces, and as wafer edge rings.

## SUMMARY OF THE INVENTION

The invention provides improved methods for manufacturing rings using chemical vapor deposition. In certain embodiments, cylindrical tubes are used as substrates and the resulting material that is deposited on and then removed from the inside surface of the cylindrical tubes can be sliced or cut into the desired ring size and shape. The resulting ring has a diameter in a planar direction and a height in a normal direction. The crystalline grains are oriented in the planar direction, and in certain embodiments, are oriented radially in the planar direction, as opposed to the perpendicular or axial growth orientations seen in the prior art rings. Put another way, the primary direction of crystal growth in materials according to the invention is in the plane of the resulting article; in the case of ring, hoop, or disc shaped articles, the primary direction of crystal growth and grain orientation is in the radial direction.

The invention also relates to methods of forming disk-shaped rings by chemical vapor deposition by

- (a) providing a round cross-sectional tube in a deposition zone;
- (b) directing precursor gas into the tube;
- (c) chemically reacting the precursor gas to form a solid deposit in the shape of the tube on the inside on the tube;
- (d) removing the solid deposit; and
- (e) dividing the solid deposit into substantially flat rings.

Advantages of this invention include increased space utilization, reduced unit cost of manufacturing the rings, reduced waste during manufacture, and the ability to

produce rings of varying diameter, cross-sectional width and thickness depending on the height of cutting (i.e., without varying the deposition time).

The invention is described in more detail below using silicon carbide as a convenient and commercially important example. However, it should be recognized, as it has been by the inventors, that articles according to the invention may be made by practicing the process of the invention using any material that can be deposited by CVD. Illustrative, non-limiting examples include oxide, nitride and carbide ceramic materials including but not limited to aluminum nitride, aluminum oxide, aluminum oxy-nitride, silicon oxide, silicon nitride, silicon oxy-nitride, boron nitride, boron caride, and other materials such as zinc sulfide, zinc selenide, silicon, diamond, diamond-like carbon, and any other material that can be prepared using CVD techniques.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a schematic of a CVD apparatus suitable for use in practicing the invention.

Figure 2 is a perspective view of a round cross-sectional tube for use with the CVD apparatus of Figure 1.

Figure 3 is a side perspective schematic view of a segmented graphite tube showing the gas injection flow through the tube.

Figure 4 is a schematic view of the material formed by deposition on the inside of the tube of Figures 2 and 3 as it is being sliced.

Figure 5 is a schematic view showing the crystal growth of a ring formed by the methods of the prior art.

Figure 6 shows the crystal growth of a ring formed by the methods of present invention.

Figure 7 is a top view schematic showing the crystal growth of a flat ring formed by the methods of present invention.

Figure 8 is a schematic showing an alternate CVD apparatus suitable for use in practicing the invention.

Figure 9 is a schematic showing SiC ring blanks used to prepare bars for MOR testing.

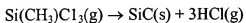
Figures 10a and 10 b are optical bright field micrographs of etched samples of material made according to one embodiment of the invention.

## DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

The largest market for SiC sheets is in the semiconductor market, which uses the high stiffness to weight ratio, chemical and physical compatibility and purity to make fixtures to support silicon and other wafers for processing. Many of these fixtures are shaped as rings, typically less than 0.2" in thickness and up to about 14" in diameter. The inner diameter is adapted to hold semiconductor wafers.

Although articles made according to the techniques described below are primarily ring-shaped, it is understood that they may have any desired shape, depending upon the size and the shape of the substrate used to form the article. For ease of discussion, however, the below description refers to flat ring-shaped articles and methods of forming the ring-shaped articles using a cylindrical tube as the substrate.

The chemical vapor deposition (CVD) process for silicon carbide (SiC) is generally based upon a thermally induced reaction within a reduced pressure, resistance heated graphite furnace. Certain embodiments of the invention use this equation and these basic parameters:



Deposition temperature: 1300 - 1400°C

Deposition pressure: ~200 torr

Catalyst: H<sub>2</sub>

Instead of using flat sided or four sided boxes for deposited material to form a sheet conforming to the dimensions of the sides of the boxes, the invention provides at least one round cross-sectional tube, the internal dimension of which accommodates the outer diameter

of the desired ring size. (If a triangular, oblong, oval, octagonal, or any other shaped article is desired, it is also possible to use tubes having the corresponding cross-section, although it is preferred that instead of sharp corners, the substrates have rounded edges to provide a more uniform distribution and to reduce internal stresses.)

The apparatus used in the process of the present invention is a chemical vapor deposition (CVD) chamber designed to deposit ceramic material on the inside of a cylindrical or tubular mandrel. Figure 1 is a schematic diagram that shows a CVD system that includes a furnace chamber 10, a gas distribution system 12 in fluid communication with the furnace chamber 10, a pumping system 14 in fluid communication with the gas distribution system 12, a power supply 16, and an effluent treatment system 18. The gas is pumped into and out of one or more box substrates 19.

In this embodiment, the invention uses as a substrate a round or circular cross section cylindrical tube 20, as shown in Figures 2 and 3. The cylindrical tube 20 is typically mounted in a vertical direction in the chamber 10, although it could be mounted at any other angle.

In use, reactant gas is admitted at an injector (shown schematically at 30) at the top of chamber 10 (although it could come in from the bottom) and into cylindrical tube 20. The gas is removed by an exhaust port (shown schematically at 32) at the bottom of chamber 10 (although it could be at the top) which connects to the pumping system 14 and effluent treatment system 18.

In this embodiment, the cylindrical tubes 20 are preferably graphite tubes that are attached in a non-rotating manner in chamber 10. Cylindrical tubes 20 may be



attached such that they are allowed or caused to rotate, but rotation is not required and is typically not employed.

The graphite cylindrical tubes 20 have a substantially round cross-section, such that the material deposited on the inside of the tubes is formed in a corresponding round cross-sectional shape. The circular radius of cylindrical tubes 20 allows uniform distribution and flow of gases.

A cylindrical tube 20 that forms the substrate for the deposition process is shown in Figures 2 and 3. Tube 20 can be a single, full length tube, or it may be a series of tube sections 24 as shown in Figure 3. If the tube is graphite, which is typically used for the SiC CVD process, a full length tube will be quite heavy and difficult to work with. Thus, one option is to provide a tube that is actually a series of tubes, for instance, four or five tubular sections, that can be attached with a joining fixture. Because the resulting deposit that is formed will be sliced or otherwise sectioned, the joints between the tube sections need not be seamless. In fact, the joining fixture may be a device that provides an indentation between the tube segments that acts as a deposition inhibitor so that the tube segments can be readily separated from one another. While any length of tube or the segments can be used, in certain embodiments, the tube segments 24 are about twelve inches high and about three to six segments are attached to one another, yielding a cylindrical silicon carbide deposit that is about 40 to about 60 inches high.

The tube 20 can have the same cross-sectional dimensions throughout, or the cross-section can be varied. For example, if the deposition tends to be greater at certain areas of the cylinder than at others, the geometry of the cross-section can be varied to accommodate those deposition variations. The cylinder can also be tapered if differently-shaped disks are

desired. Alternatively, the cylinder can be terraced or stepped to provide clear divisions between the sections.

During processing, precursor gas is fed into the internal diameter of the cylindrical tube 20 in order to make a tubular monolith of CVD deposited material, such as a ceramic material. In the illustrated embodiment, gases are fed at the top of the chamber through injector 30 and exhausted at a manifold or exhaust port 32 at the bottom of the chamber. Each of the cylindrical tubes 20 has a dedicated, independent injector or precursor gas feed positioned so that the gas enters at one end 26 of cylinder and exits through the other end 28. This allows deposition primarily on the surfaces of interest only, the internal diameter 22 of the tube 20, and not on other surfaces, such as the outside of the cylindrical tube 20. The gas travels in a path along the axis of the tube. This provides a more efficient deposition process by allowing better control of gas conditions. The only asymmetry in thickness that may arise is a thickness gradient from the top to the bottom of the tube, although the thicker areas can be machined to the proper thicknesses.

In certain specific embodiments, the gas feed is a linear, symmetrical chemical vapor deposition system with reaction gas entering the chamber approximately at the center of the diameter such that the gas is deposited substantially evenly along the inside surface 22 of the tube 20. The reaction product is deposited to a set thickness on the internal surface. The SiC builds up on the inner surface of the tube in a substantially radial direction, as shown by Figures 6 and 7.

This process is more efficient than the prior art process in which reaction products are deposited throughout the chamber and not at specific locations. The cylinder also does not

need to be rotated in order to obtain the desired uniform deposition in a consistent manner, in contrast to many methods of the prior art, although it could be rotated if desired.

Typically, the deposition thickness is approximately 1 inch, although a wide range of material thickness from approximately 0.1 inch to over 2 inches may be obtained by varying gas flow rates and deposition times. Gases from multiple tubes may be evacuated commonly from the chamber through exhaust port 32.

Once the silicon carbide has been deposited on the inside of the tubular mandrel, the deposit is removed from the mandrel by any appropriate technique, including, but not limited to grinding or electrical discharge machining. A release coating or other substance may be applied to the inner surface of tube for ease of removal.

The resulting SiC tube can be cut through the circular cross section to yield a ring or a hoop, as shown in Figure 4. Cutting can be accomplished by using ceramic machining techniques including, but not limited to, diamond slicing, ultrasonic cutting or laser cutting. In the case of using an electrically-conductive deposited material, electrical discharge machining can be used to slice rings from the tubular section.

Rings of varying diameter can be produced by varying the cross-sectional width and thickness of deposition to give the desired internal diameter. Overall height of the ring can be adjusted by varying the height of cutting.

The outer diameter of the ring or hoop will correspond to the inner diameter of the cylindrical tube 20 and the inner diameter of the ring or hoop will depend upon the amount of gases that are fed through the tube and allowed to deposit. The thicker the deposit, the smaller the inner diameter of the ring that can be produced. The diameters of the ring may then be machined, smoothed or otherwise shaped to provide the desired dimensions.

An alternate embodiment that may be used to form rings is shown in Figure 8. In this embodiment, a rod is disposed within the cylindrical tube, and material is caused to deposit both on the inner surface of the tube as well as on the outer surface of the rod. This method may produce two differently-sized rings; one ring that corresponds to the inner diameter of the cylinder and another ring that corresponds to the outer diameter of the rod.

Rings sliced from cylinder deposits of this invention are easier to machine than rings made using the methods of the prior art due to the lower internal or out-of-plane stresses around the ring. Generally, as material is deposited via CVD, there are subtle but unintentional variations in the process parameters that can affect the nature of the material and the crystal growth structure can vary, creating inherent stresses in the material. These stresses can cause bowing or bending in rings that are cut out of a sheet of material with the predominant direction of crystal growth in the direction normal to the plane of the sheet. By contrast, the symmetry provided by using a cylindrical tube mandrel or support according to the invention affords a substantially symmetrical stress gradient around the ring, so that any inherent stress exhibited on one side of the ring is balanced by a similar inherent stress on the opposite side of the ring (i.e., there is no net stress in the plane of the ring). In other words, the inherent stress is directed inwards or outwards in a similar manner, affecting the ring or disk in a substantially symmetrical way.

For SiC that is deposited upon a flat surface, the stress gradient on the lower surface 44 will be different from the stress gradient on the upper surface 46 due to the way the ring is manufactured. This can cause the material to bend or bow, preventing the manufacture of a flat ring.

By contrast, for SiC that is deposited within a cylindrical tube, the stress gradient difference is exhibited between the outer surface 48 and in the inner surface 50, such that any stress gradient “squeezes” the ring symmetrically. Accordingly, rings that are cut from the resulting cylindrical deposition have substantially uniform properties around them due to the uniformity of the deposition parameters across that particular slice. (However, it is possible that properties of slices cut from different positions along the cylinder will be slightly different due to the different deposition parameters along the particular length of the cylinder.)

If the cylindrical tube 20 is provided as a series of sections, the deposit can be removed by disassembling the sections. Even if the resulting deposit fractures or cracks, the cracked areas do not cause a great deal of wasted material because they will typically be across the diameter of the material due to the microcrystalline structure of the material. This is the portion of the ring that will be machined during cutting or slicing.

During the prior art deposition process (whether the ring is formed from a flat sheet or on a ring shaped mandrel), the growth direction of the crystal structure is in the direction of the height 40 of the ring, as shown in Figure 5. This is the case whether the deposit is formed on a flat graphite sheet, on a series circular mandrels mounted on a shaft, or on graphite rings suspended in the chamber.

However, rings according to the present invention exhibit the growth direction of the crystal structure in the direction of the length 42 or diameter of the ring, as shown in Figures 6 and 7. In other words, the crystal growth forms on the inside of the cylindrical tube 20 and extends inward in a substantially radial manner. When the resulting cylindrical deposit that is formed is removed from the tube, it will have a long axis and a circumference. The growth

of the crystal grain is around the radial circumference and perpendicular to the long axis. Once the cylindrical deposit is sliced or cut into individual rings, the grains are oriented in the plane of the finished article. This is directly contrary to the crystal growth seen in rings that are manufactured using traditional methods.

In one embodiment of the method of the present invention, free-standing silicon carbide tubes from which the rings are sliced are deposited from a mixture of silicon carbide precursor gases, such as a mixture of methyltrichlorosilane (MTS) and hydrogen, with an optional inert gas, such as argon or helium and optional dopant gas into a deposition chamber heated to a temperature typically between 1300°C and 1400°C. Deposition pressure is maintained at approximately 100 torr to 300 torr. The relative partial pressure flow ratio of hydrogen to MTS is maintained in the range of approximately 5 to 10.

Reaction gases are delivered into a tubular mandrel through a single injector or an array of injectors positioned symmetrically at either the top or bottom. Under these conditions, silicon carbide is deposited on the inside of the tubular mandrel(s) at a deposition rate of approximately 1 to 2  $\mu\text{m}/\text{minute}$  and the deposition process is continued until the desired thickness of SiC material is achieved. Typical deposition periods vary between 50 and 300 hours.

Upon completion of the deposition, the mandrel and deposit are removed from the reaction chamber and with or without first separating the mandrel from the deposited material, the silicon carbide rings are sliced from the tube. The outer and inner dimensions and the thickness of the ring are then machined to specification using diamond grinding methods.

The unique characteristics of the products of the present invention, i.e. low in-plane residual stress, extreme flatness, high control of machinability, allow for the manufacture of very thin (e.g. less than 0.5 inch) hoop-shaped rings, and more complicated rings with or without bulk “drop-offs.”

## **EXAMPLES**

Using the process of the present invention, 200 mm and 300 mm diameter SiC edge rings for Si wafer processing have been produced and characterized. Rings were made from both electrically insulating CVD-deposited SiC material exhibiting a typical electrical resistivity of about 100 to 10,000 ohm-cm, and electrically conductive SiC with an electrical resistivity of less than 0.01 ohm-cm.

In the following Examples, flexural strength measurements, also known as modulus of rupture (MOR) tests, on the deposited SiC materials were obtained using the 4-point bend test according to ASTM C-1161. The MOR test samples (bars) were cut from rings sliced from the deposited cylinders. The MOR bar samples had the following dimensions: length of 45 mm, width of  $4 \pm 0.13$  mm, thickness of  $3 \pm 0.13$  mm, edge chamfer of  $0.12 \pm 0.03$  mm at an angle of  $45^\circ \pm 5^\circ$ . Chamfers were fabricated by grinding with a 600-grit grinding wheel, while the large planar sides of the MOR bars were finished with a 320-grit wheel. The approximate layout of the MOR bars 9a cut from the SiC ring blank 9b is shown in Figure 9. The 44 mm x 4 mm side of the MOR bar was obtained from the plane of the ring.

Electrical resistivity measurements were made with a Jandel Company hand held 4-point probe, consisting of a linear array of 4 points spaced 1 mm apart. The

resistivity was calculated assuming an infinite material thickness. Three data sets were obtained at each of four measured positions on each sample ring.

### EXAMPLE 1

SiC edge rings for handling 300 mm Si wafers for semiconductor processing were fabricated as follows. A graphite tube with nominal inner diameter of 340 mm was manufactured from an isostatically pressed, fine grained grade of graphite with a thermal expansion similar to that of dense CVD SiC. Four tubular sections, each with a length of approximately 13 inches were assembled in a CVD reactor. Optional deposition-prohibiting spacer devices were positioned in between each section to facilitate removal of each tubular section after deposition.

The precursor gas MTS was introduced through a single injector positioned symmetrically at the top of the tubular mandrel assembly at a flow rate of 9.1 liters per minute. Hydrogen was delivered through the same injector at a flow rate of 76 liters per minute. The ratio of hydrogen-to-MTS was 8.4. The CVD reactor pressure was 200 torr and deposition temperature was 1350°C. The total deposition time was 174 hours, and the average deposition rate of the SiC material was 0.05\_inch per hour.

After deposition, the reaction chamber was opened and the tubular mandrels, spacer devices and tubular SiC deposits were removed. Each of the tubular deposits was then sliced using a diamond abrasive slitting wheel into ring slices having a thickness of approximately 0.2 inch. These slices were then ground to the final edge ring specification.

The SiC material deposited by this technique had a density of 3.21 g cm<sup>-3</sup>, Vickers hardness >2700kg mm<sup>-2</sup> and thermal conductivity between 240 and 270 Wm<sup>-1</sup>



$^{\circ}\text{K}^{-1}$ , and an electrical resistivity between 390 and 450 ohm-cm. These measurements are in the same range as Jandel probe resistivity measurements obtained from plate-form SiC material that has been deposited under similar conditions, but on flat graphite sheets.

The flexural strength of rings obtained by this process varied between 40 and 65 ksi (275 to 450 MPa), depending upon where the ring was sliced from the tubular deposit. Figure 10 presents bright field optical micrographs of an etched sample obtained from a ring which exhibited a flexural strength of 62 ksi. The lower portion of Figure 10 (a) is the outer diameter of the ring slice, which is part of the deposit that was next to the graphite mandrel substrate. The upper portion of Figure 10 (b) shows a portion of the deposited material taken from a point 13.2 mm from the substrate, i.e. the SiC deposit was 13.2 mm thick. The increase in grain size within the SiC deposit as the distance from the substrate is increased is clearly noticeable, as is the orientation of the grains as illustrated in Figure 6.

For comparison, SiC material deposited in plate form that has been deposited under similar conditions onto flat graphite sheet exhibits a flexural strength in the range of 47 to 70 ksi (320 to 480 MPa). That the rings of the present invention with a SiC grain growth orientation parallel to the plane of the ring had a flexural strength equal to that of rings made from SiC material with grain growth orientation perpendicular to the plane of the ring was surprising. This excellent result was unexpected since in the flexural strength test of the material of the present invention, the SiC material is bent in a direction parallel to the direction of grain growth, i.e. using an analogy to wood, the material is bent "along the

direction of the grain.” Therefore, the present invention overcomes prior art deficiencies associated with fabrication of ceramic rings, while maintaining outstanding material strength.

## **EXAMPLE 2**

SiC edge rings for handling 200 mm Si wafers for semiconductor processing were fabricated according to the process of Example 1, with the following exceptions: the graphite tube had a nominal inner diameter of 240 mm, each tubular graphite section had a length of approximately 9 inches, and the hydrogen-to-MTS flow ratio was 7.4. The average deposition rate was 0.051 inch per hour. The flexural strength of rings obtained varied between 57 and 68 ksi (390 to 465 MPa), again indicating outstanding material strength.

## **EXAMPLE 3**

SiC edge rings for handling 200 mm Si wafers for semiconductor processing were fabricated according to the process of Example 2, with the following exceptions: each tubular graphite section had a length of approximately 8.5 inches, and the hydrogen-to-MTS flow ratio was 8.4 and a doping gas was added to produce an electrically conducting SiC deposit. The average deposition rate was 0.065 inch per hour. Rings obtained varied in electrical resistivity from 0.004 ohm-cm to 0.007 ohm-cm.

For comparison, SiC material deposited in plate form that has been deposited under similar conditions onto flat graphite sheet typically exhibits a resistivity between 0.002 ohm-cm and 0.008 ohm-cm. Therefore, the electrical resistivity measurements obtained from the deposit in Example 3 are similar to measurements obtained from plate-form SiC material deposited under similar conditions.

Representative rings from the prior examples have been coated with CVD silicon coatings to reduce opacity to light and to provide a high purity Si surface for contact to Si

wafers during wafer processing. Typically, this deposition is conducted at or near atmospheric pressure using trichlorosilane as a source of silicon and a CVD temperature of between about 1000 °C and 1200 °C. Other vacuum deposition and vapor deposition methods including but not limited to evaporation, sputtering, ion plating, ion beam deposition and plasma deposition can be used to deposit coatings over the products of the present invention. Because of the orientation and uniform nature of the microstructure of the material of the present invention, coatings applied to the products of the present invention have improved cosmetic appearance compared with coatings applied to prior art CVD products.

In addition to the excellent material properties summarized above, additional unexpected benefits have been found with regard to processing the materials of the present invention. In addition to providing materials having better stress distributions and flatter profiles, the method of the present invention also increases manufacturing capacity significantly by allowing multiple cylindrical deposition chambers inside one CVD furnace, replacing at least one of the conventional squared-sectioned box sites or flat mandrels with at least one cylindrical tube. In addition, other time and cost savings are realized by use of the process of the invention.

First, when compared to fabrication of rings from plate-form CVD SiC material, the fabrication time of product of the present invention is significantly less. Typical fabrication, i.e. cutting or slicing the ring from the deposit, then grinding to final dimensions, is reduced by approximately 35%.

Also, because the rings are flat as sliced from the tubular deposit, grinding to the specified ring flatness of 0.002 inch can be achieved on the first attempt with the

product of the present invention. In contrast, plate-form deposited SiC material has a characteristic bow that must be machined out to achieve a final flat part. Multiple processes of alternate side grinding are required with plate-form SiC, and the first grinds are outside of flatness specification by several thousandths of an inch.

It has also been surprisingly found that the process of the present invention produces a material that is very uniform and provides consistent results during grinding, when compared to plate-form material. The plate-form SiC material is often inconsistent in thickness and uniformity across the dimension of a ring, and requires significant machine operator judgment and adjustment to produce finished parts within the desired product specifications. In addition, it is believed that the nonuniform machining of the plate-form material can induce unwanted stresses. Because of the uniform microstructure in the axial direction, and because of the grain orientation of the present invention, the material grinding to final configuration is much more consistent.

Although the specific examples presented above are for CVD silicon carbide materials, similar results are anticipated with other materials that can be deposited by CVD including, but not limited to other oxide, nitride and carbide ceramic materials such as aluminum oxide, aluminum nitride, aluminum oxy-nitride, silicon oxide, silicon nitride, silicon oxy-nitride, boron nitride, boron carbide, and other materials such as zinc sulfide, zinc selenide, silicon and diamond.

What is claimed is:

1. A structure formed by chemical vapor deposition having a planar direction and a normal direction, wherein the structure has a dimension in the planar direction that is larger than the dimension in the normal dimension and having grains substantially oriented in the planar direction.
2. The structure of claim 1, wherein the structure is a flat ring having a circumference and wherein the grains are oriented in a substantially radial direction around the circumference of the ring.
3. The structure of claim 1, wherein the structure comprises silicon carbide.
4. The structure of claim 1, wherein the structure is a ring that comprises an inner diameter and an outer diameter and wherein the distance between the inner diameter and outer diameter is approximately one inch.
5. The structure of claim 4, wherein the inner diameter is between about 100 mm to 600 mm in diameter.
6. The structure of claim 1, having an axial thickness of between about 0.2 inches to fourteen inches.

7. The structure of claim 1, wherein the structure is a flat ring that has a curved outer surface.
8. The structure of claim 1, wherein the structure is a flat ring having a circumference that has substantially symmetrical stresses around the circumference of the ring.
9. The structure of claim 1, further comprising a layer of silicon deposited on at least one surface thereof.
10. A method of making flat rings by chemical vapor deposition, comprising:
  - (a) providing a round cross-sectional tube in a deposition zone;
  - (b) directing precursor gas into the tube;
  - (c) chemically reacting the precursor gas to form a solid deposit in the shape of the tube on the inside on the tube;
  - (d) removing the solid deposit; and
  - (e) dividing the solid deposit into substantially flat rings either before or after removal.
11. The method of claim 10, wherein the precursor gas comprises methyltrichlorosilane.
12. The method of claim 10, wherein the tube comprises a graphite tube.

13. The method of claim 10, wherein the deposit comprises silicon carbide.
14. The method of claim 10, wherein the tube is provided as a plurality of segments.
15. The method of claim 10, wherein the dividing comprises slicing the deposit into flat rings having an axial thickness of between about 0.2 inches and about fourteen inches.
16. The method of claim 10, further comprising (f) machining the substantially flat rings to desired dimensions.
17. The method of claim 10, wherein the ring has a planar direction and a normal direction with the dimension in the planar direction being larger than the dimension in the normal dimension, and wherein grains of the ring that are deposited by chemical vapor deposition are substantially oriented in the planar direction.
18. The method of claim 17, wherein the ring has a circumference and wherein the grains are oriented in a substantially radial direction around the circumference of the ring.
19. The method of claim 10, wherein several tubes can be positioned within a CVD furnace.

20. The method of claim 10, further comprising applying a coating of silicon to at least one surface of the ring.

21. The method of claim 20, further comprising machining the ring prior to applying the silicon coating.

22. The method of claim 20, wherein the silicon coating is applied using chemical vapor deposition.



### **ABSTRACT OF THE DISCLOSURE**

Improved methods for manufacturing rings using chemical vapor deposition. Cylindrical tubes are used as deposition substrates and the resulting material deposited on the inside surface of the cylindrical tubes is sliced or cut into the desired ring size and shape. The resulting rings have a crystal growth that is oriented substantially planar to the finished article.

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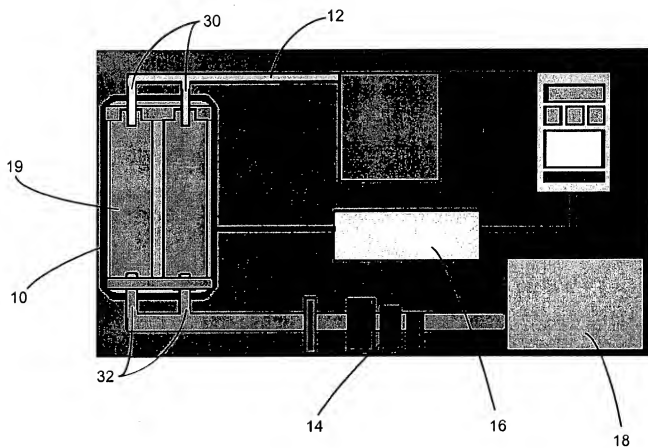


FIGURE 1

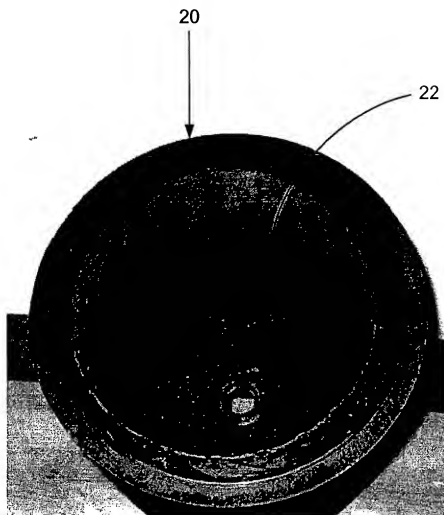


FIGURE 2

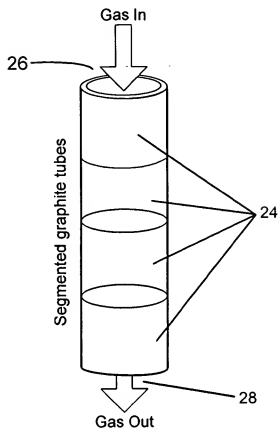


FIGURE 3

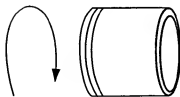
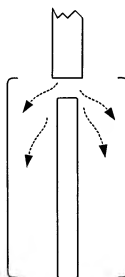
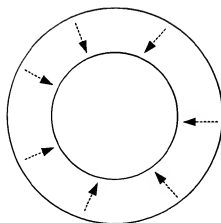
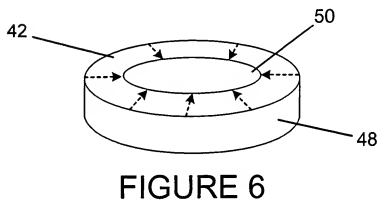
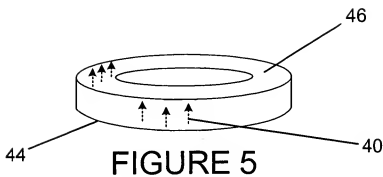


FIGURE 4



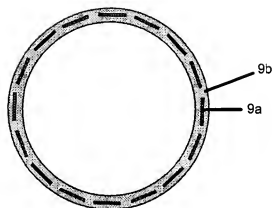


FIGURE 9

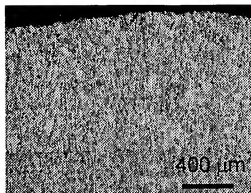


FIGURE 10a

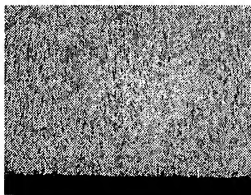


FIGURE 10b



**DECLARATION FOR PATENT APPLICATION**☒ Original☐ Supplemental☐ Substitute☐ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below), or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a design patent is sought on the invention entitled:

**ARTICLES FORMED BY CHEMICAL VAPOR DEPOSITION AND METHODS FOR THEIR MANUFACTURE**

(Title of the Invention)

the specification of which (check one)

☒ is attached hereto☐ was filed on \_\_\_\_\_

and was amended \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a) - (d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified, by checking the box below, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Applications			Priority Claimed		Copy Attached	
Application Number	Country	Foreign Filing Date (MM/DD/YYYY)	YES	NO	YES	NO

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below and claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT international application(s) designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

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Inventors : David Forrest and Mark Schauer

For: ARTICLES FORMED BY CHEMICAL VAPOR DEPOSITION AND METHODS FOR THEIR MANUFACTURE

Filed: December 5, 2003

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Declaration for Patent Application

Page 2

Parent Application Number	Filing Date	Status (Mark Appropriate Column Below)		
		Patented	Pending	Abandoned

As a named inventor, I hereby revoke all prior powers and appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

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Inventors : David Forrest and Mark Schauer

For: ARTICLES FORMED BY CHEMICAL VAPOR DEPOSITION AND METHODS FOR THEIR MANUFACTURE

Filed: December 5, 2003

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Page 3

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Full name of sole or first inventor David Forrest

Inventor's signature \_\_\_\_\_ Date \_\_\_\_\_

Residence \_\_\_\_\_

Citizenship \_\_\_\_\_

Post Office Address \_\_\_\_\_

Full name of second inventor Mark Schauer

Inventor's signature \_\_\_\_\_ Date \_\_\_\_\_

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Citizenship \_\_\_\_\_

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